

1048.026



PATENT SPECIFICATION

NO DRAWINGS

1048.026

Date of Application and filing Complete Specification: May 3, 1963.

No. 17568/63.

Application made in United States of America (No. 192,342) on May 4, 1962.

Complete Specification Published: Nov. 9, 1966.

© Crown Copyright 1966.

Index at acceptance:—C3 G(1BX, 2C, 4A, C); C3 P(7C13B, 7C13C, 7D2A1, 7T2D, 7T2X)

Int. Cl.:—C 08 f 25/00

COMPLETE SPECIFICATION

Ion Exchange Materials

We, AMERICAN MACHINE & FOUNDRY COMPANY, a corporation of the State of New Jersey, United States of America, of 261 Madison Avenue, New York 16, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to molded and otherwise shaped thermoplastic products and specifically to those constituted of a plurality of different ion-exchange materials randomly mixed together.

It is well-known to make shaped articles by mixing together finely ground ion-exchange resins and a thermoplastic binder and forming the mixture into an article such as a sheet or membrane. In known articles the ion-exchange material has been either anion or cation exchange resin, but not a mixture of both types. Membranes made by holding together particles of resin with an inert binder are known as heterogeneous and display two distinct phases in that the particles can be picked out of or distinguished within the adhesive matrix.

It is also known to make shaped articles from a single kind of ion-exchange material, such as cation-exchange material, in which the material is in a single continuous phase. Generally these are nearly transparent. Such articles are considered to be homogeneous.

Ion-exchange materials are also known which are homogeneous thermoplastic polymers. Graft copolymers of polyethylene and styrene sulfonic acid, for example, are formed as ion-exchange particles which are pressed together as sheets or membranes in Patent Specification 926,477.

Previously it has been known to make shaped articles containing ion-exchange groups of either the cation-exchange or anion-exchange

category, but prior to this invention no shaped article was known containing random, multiple, synthetic, organic, thermoplastic ion-exchange materials of both categories.

None of the prior ion-exchange manufactures have included both anion and cation-exchange properties. Such a combination of properties is useful in a battery separator, for example. As membranes these materials may also be used as non-selective or low selectivity ion permeable barriers in electrodialysis and in pressure dialysis or in fuel cells.

According to the present invention we provide a method of making a composition of matter comprising mixing together at least two ion-exchange materials, one of which is predominantly a cation-exchange material and another of which is predominantly an anion-exchange material, and the ion-exchange materials are organic polymers which are ion conductive in an electric field, and at least one of said polymers is thermoplastic, to form a random mixture and thereafter subjecting said mixture to pressure at a temperature at which the thermoplastic material bonds the ion-exchange materials together into an integral self-supporting mass. When particles of ion-exchange mixed polymer materials are pressed together and heated, or are treated on the surface at least with a solvent which partially softens them, they may be formed into useful shaped articles. The structure of the article is generally homogenous and shows a continuous translucent phase. The articles themselves may be further shaped or welded together to make larger forms; and openings and cracks may be patched by welding. Ions of both signs will be conducted through the articles when they are used as barriers between electrolyte solutions in an electric field. By varying the proportions of negative and positive resin it is possible to control ion transport selectively.

For the purpose of the invention it is possible to use any organic polymers which can

[Pri

be mixed in particulate form and caused to adhere together to form a mechanically coherent composition.

5 The particulate material may have a mesh size of 15 to 75 United States of America Standard mesh size.

10 The composition is ion-conductive and may be ion-selective when a preponderance of either cation or anion material is used to make it. Additional plasticizer, reinforcement such as fibers, or dye material may be included in the composition, but generally extra adhesive is not used. However, when polyethylene base ion-exchange material is used, 15 it is sometimes useful to include a minor amount of other polyolefin material such as tetrafluoroethylene in order to impart chemical stability or heat stability and also to dilute the exchange capacity. It is also useful to mix 20 particles of different polymer types such as polyethylene styrene sulfonic acid with polytetrafluoroethylene styrene sulfonic acid. Such a mixture combines the chemical resistance of the fluoropolymer and the easier bonding properties of polyethylene.

25 By a mechanically coherent random mixture is meant that the constituent ingredients are associated with each other so that they hold together without necessarily being arranged in any particular pattern and are self-supporting in useful shapes and sizes.

30 A predominantly cation-exchange material may contain some anion-exchange groups in low proportion to cation-exchange groups and vice versa.

35 The present invention includes only organic polymers as the ion-exchange material. This material when used as a barrier between two aqueous electrolyte solutions is ion-conductive when a direct electric current is impressed across it and the solutions. Accordingly, ion-exchange groups extend throughout the material, since if they were present only in surface layers, the inert interior would block 40 movement of ions and serve as an electrically insulating barrier.

45 An integral self-supporting mass can be shaped and formed and is substantially impervious to fluid except for local swelling and ion shell transport including for example water of hydration. The thermoplastic material seals the interstices between areas of ion-exchange material so that fluid does not flow or diffuse therebetween.

EXAMPLE I

55 A cation-exchange material is made by placing polyethylene resin particles of density 0.92 in monomer-grade styrene free from polymerization inhibitor and containing a catalyst viz. 0.05% benzoyl peroxide and heating the suspension at 75°C. until the particles have 60 increased in weight by about 25 per cent. Whereupon the particulate graft copolymer so formed is separated, from the styrene, washed 65 with ethylene dichloride, and then treated with

a 10 per cent solution of chlorosulfonic acid in ethylene dichloride at 25° for two hours. After a second washing in ethylene dichloride the particles are air-dried and then hydrolyzed in 5 per cent aqueous sodium hydroxide for about 18 hours. The cation-exchange particles so formed are then washed in water and dried. 70

Anion-exchange material is made from the same copolymer by treatment of the cation-exchange material with 15 per cent stannic chloride and 5 per cent paraformaldehyde in chloromethyl methyl ether for one hour at 75°, washing with ethylene dichloride, treatment with 20 per cent aqueous trimethylamine for 18 hours, followed by washing with 5 per cent hydrochloric acid, and washing with water. 80

Material made according to specification Patent 926,477 may be substituted for the above. 85

Finely divided pieces of the two materials made above are air dried and then 10 parts of each are intermixed. The mixture is placed on one piece of aluminum foil, patted down to form a layer about 0.01 inches thick, and covered with another piece of aluminum foil. The wrapped layer is placed in a laboratory press at 150°C and then subjected to 1000 psi for two minutes. A clear self-supporting film of flexible amphoteric ion-exchange membrane is thus made. Pressure may range up to about 15,000 psi. 90 95

EXAMPLE II

Seven parts of the cation-exchange material of Example I, two parts of the anion-exchange material of Example I, and one part of polyethylene pellets of 0.92 density and a melt index of 10-15 are thoroughly intermixed and by the method of Example I subjected to 1000 psi for three minutes at 160°C. in a mold to form a molded article in the form of a disc having holes and projections for mechanical mounting. 100 105

EXAMPLE III

Seven parts of the cation-exchange material of Example I (30 mesh) and three parts of a porous polystyrene quaternary amine ion-exchange resin available from the Rohm and Haas Co. of Philadelphia, Pa., as Amberlite (Registered Trade Mark) IRA-401 of about 20 to 50 mesh are thoroughly mixed and subjected to 1000 psi for five minutes at 175°C by the method of Example I and formed into a sheet. 110 115

WHAT WE CLAIM IS:—

120 1. A method of making a composition of matter comprising mixing together at least two ion-exchange materials, one of which is predominantly a cation-exchange material and another of which is predominantly an anion-exchange material, and the ion-exchange materials are organic polymers which are ion conductive in an electric field, and at least one of said polymers is thermoplastic, to form a random mixture and thereafter subjecting said 125 130

mixture to pressure at a temperature at which the thermoplastic material bonds the ion-exchange materials together into an integral self-supporting mass.

5 2. A method according to claim 1 in which the separate ion-exchange materials are provided in the form of particles.

10 3. A method according to any of the preceding claims wherein at least one polymer is made by chlorosulphonating polyethylene particles that have been treated with monomeric styrene and a catalyst.

4. A method according to any of the preceding claims in which the integral self-supporting mass is shaped into a film to form an ion-exchange membrane. 15

5. A method as claimed in claim 1 substantially as hereinbefore described.

For the Applicants:
MATTHEWS, HADDAN & CO.,
Chartered Patent Agents,
31/32, Bedford Street, Strand,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.